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COMPOSITIONS FOR WATER-ABSORBING SHEETS

Inventors: Kozo Mita

Dainippon Printing Co., Ltd.
1-1-1 Ichitanikoga-cho, Shinjuku-ku,
Tokyo

Junichi Kuroki
Dainippon Printing Co., Ltd.
1-1-1 Ichitanikoga-cho, Shinjuku-ku,
Tokyo

Applicant: Dainippon Printing Co., Ltd.
1-1-1 Ichitanikoga-cho, Shinjuku-ku,
Tokyo

Agents: Yoshisuke Hiraki, patent attorney;
and one other

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Claims

1.Compositions for functional water-absorbing sheets, characterized by containing at least a water-absorbing material, a specific functional material, and a binder if needed.

2.Compositions described in Claim 1, wherein the functional material is an antibacterial material obtained by impregnating an antibacterial agent in a carrier.

3.Compositions described in Claim 1, wherein the functional material is a deodorant.

4.Compositions described in Claim 1, wherein the functional material is a bromine-adsorbed carbon molecular sieve having micropores of 4-6Å.

5.Compositions described in Claim 1, wherein the functional material is obtained by dissolving sodium bromate or potassium bromate in acidic water, adding it to activated carbon, reacting, and drying.

6.Compositions described in Claim 1, wherein the binder is a thermoplastic resin.

7.Compositions described in Claim 1, characterized by comprising water-absorbing resins and paints or printing ink containing a functional powder.

Detailed explanation of the invention

Industrial application field

The present invention relates to compositions for water-absorbing sheets having functionality, more specifically, compositions for water-absorbing sheets provided with the specific function of being useful as materials for products requiring high water absorptivity such

as freshness-maintaining materials of fresh food, sanitary products, diapers, disposable mops, paper towels, etc.

Prior art

Until now, water-absorbing resins have been widely used as materials for freshness-maintaining materials of fresh food, sanitary products, diapers, disposable mops, paper towels, etc.

Various measures have been taken for maintaining the freshness in the case of fresh food, but since free water exuded from fresh food, especially meat, fish, etc. notably lowers the freshness of the food, the immediate removal of the free water is an important factor, which cannot be neglected in the maintenance of the freshness.

As a measure for countering this free water, a method of putting water-absorbing sheets made from water-absorbing polymers in the fresh food package is known as one technique.

In addition, for vegetables and fruits, freshness is lowered by ethylene gas generated in a sealed state, such as being packaged in cases or bags, or by dew condensation of water vapor by respiration.

To prevent a decrease in freshness of vegetables and fruits, a method of placing two kinds of freshness-maintaining materials, e.g., water-absorbing sheets from water-absorbing resins and ethylene gas adsorbents, in the transport mode for the vegetables and fruits, which are packaged in cases or bags, is known.

As other water-absorbing sheet products for various applications, various types such as those obtained by sandwiching a water-absorbing resin powder between two water-permeating sheets, those obtained by forming a water absorbing layer with a pattern form on the surface of a sheet using a coating material containing a water-absorbing resin while forming an adhesive layer in the non-patterned part and adhering another sheet to the former sheet, etc. have been known.

Problems to be solved by the invention

In the aforementioned prior art, however, it is necessary, for instance, in the case of packaging of vegetables and fruits to individually place two kind of materials of water-absorbing sheets and ethylene gas adsorbents in the packaging form, and in the case of packaging a large quantity of fresh food, various problems arise, such as excess labor and time, lowering of overall operation efficiency to increase costs, etc.

Furthermore, there is a risk that small bags containing ethylene gas adsorbent may break during transport, and if so, the ethylene gas adsorbent may adhere to the surface of vegetables

and fruits to deteriorate the appearance of the products, or chemical components of the ethylene gas adsorbent may contaminate the food.

Ordinary packaging materials are used in packaging of ordinary fresh food, and since the packaging materials themselves do not have specific functions, e.g., antibacterial characteristics, it is impossible to assuredly prevent a decrease in the freshness of the food, which is caused by contamination with food putrefactive bacteria, only by using water-absorbing sheets, and the establishment of an effective measure has been desired.

In addition, animal food such as meat, fish, etc. is preserved and distributed in the frozen state, but during this time, peculiar odors besides drippage are generated from food tissue, and these odors notably lower commodity values. Especially if food is once frozen and then thawed, odor generation is notable, since tissue itself is destroyed, and it is strongly desired to prevent or remove this odor.

Even in products requiring high water absorption, e.g., sanitary products, diapers, disposable mops, paper towels, etc., besides the aforementioned fresh food, effective measures are not yet sufficient regarding prevention of contamination by bacteria and deodorization in addition to water absorption, and the development of new products having specific functions to solve the aforementioned problems has been desired.

Furthermore, there is a problem of absorbed water transferring to the back surface of the water-absorbing sheets to make their handling difficult.

The present inventors assiduously conducted studies to solve the problems of the prior art in the aforementioned state and found that the aforementioned problems could be solved by water-absorbing sheets having water absorbing characteristic and specific functions, and obtained by combining a specific packaging material with a water-absorbing material and a specific composition containing a specific functional material, and the present invention was completed by this finding.

Namely, the purpose of the present invention is to provide compositions for novel water-absorbing sheets having high water absorptivity and specific functions and such sheets are useful as freshness-maintaining materials for fresh food, etc.

Means to solve the problems

The constitution of the present invention employed for accomplishing the aforementioned purpose relates to compositions containing polymers having water absorptivity and specific functional materials, and these are sandwiched between specific packaging materials to make sheet-form products. More concretely, these are as follows:

(1) Compositions for functional water-absorbing sheets, characterized by containing at least a water-absorbing material, a specific functional material, and a binder as needed.

(2) Compositions described in (1), wherein the functional material is an antibacterial material obtained by impregnating an antibacterial agent in a carrier.

(3) Compositions described in (1), wherein the functional material is a deodorant.

(4) Compositions described in (1), wherein the functional material is a bromine-adsorbed carbon molecular sieve having micropores of 4-6Å.

(5) Compositions described in (1), wherein the functional material is obtained by dissolving sodium bromate or potassium bromate in acidic water, adding it to activated carbon, reacting, and drying.

(6) Compositions described in (1), wherein the binder is thermoplastic resin.

(7) Compositions described in (1), characterized by comprising water-absorbing resins and paints or printing ink containing a functional powder.

Next, the present invention will be explained in detail based on the drawing. Figure 1 is one application example of the present invention, and it is a cross-sectional view of a water-absorbing sheet having a specific function, which is manufactured by sandwiching a deodorant-containing composition 3 between an inner layer 2 and another inner layer 4, both of which are made from paper, and packing the insert into a packaging bag prepared by an outer layer 1 and another outer layer 5, both of which are made from nonwoven fabric.

As packaging materials to form inner layers and outer layers, suitable water-permeating materials, such as water-permeating porous sheets, e.g., unsized paper, nonwoven fabric, hydrophilized polyethylene, polypropylene, etc., thermoplastic films having fine continuous pores obtained by foaming, those films obtained by adding inorganic substances or high-melting point nucleating agents and stretching to form fine continuous pores, blended paper of polyethylene or polypropylene and pulp, laminates of paper and nonwoven fabric, sized paper, those materials obtained by forming cellulose layers on nonwoven fabric using viscose, and cellulose membranes having fine pores are used and suitable water-impermeable materials such as plastic films from thermoplastic resins, PE paper, metal foils, etc. also can be used.

As nonwoven fabric, especially nonwoven fabric made from partially or wholly thermoplastic resins, e.g., rayon, pulp fiber, etc., nonwoven fabric impregnated or admixed with resins such as polyolefin, polyester, polyamide, etc., or nonwoven fabric from polyolefin, polyester, or polyamide fibers, etc. is preferably used, and fabric having a base weight of 15-100 g/m^2 is preferred.

In addition, as paper, those obtained by superposing soft paper such as tissue paper with a base weight of 15-60g/m^2 are used but the paper is not particularly restricted.

As the functional material in composition 3 of the present invention, substances or compositions having a suitable function such as an antibacterial agent, deodorant, ethylene gas

absorbent, etc. or having multiple functions by suitably combining the aforementioned functions are used.

Then, as antibacterial agents, those obtained by carrying antibacterial metallic materials such as silver, copper, zinc, tin, lead, bismuth, cadmium, chromium, mercury, etc. on carriers such as zeolite, activated carbon, silica, activated clay, acid clay, alumina, activated bauxite, bone ash, a molecular sieve, etc. are desired, but the antibacterial materials, type of carriers, and their application quantity are not particularly restricted.

As deodorants, the following are illustrated.

(1) Physically adsorbing deodorants

neutral activated carbon, fibrous carbon adsorbent, zeolite, activated alumina, acid clay, etc.

(2) Chemical deodorants

acidic agent, alkaline agent, oxidizing agent, reducing agent, etc.

(3) Physical-chemical deodorants

alkaline or acidic impregnated activated carbon, zeolite adsorbed with refined vegetable oil, etc.

(4) Others

ferrophthalocyanine derivatives, salts having a desulfurization function such as zinc oxide, mixtures of iron (II) compounds, L-ascorbic acid, alum, etc.

Besides the above deodorants, any of those having a deodorization function can be used, and they are used singly or as a mixture. The deodorants at an amount of 0.1-150 g/m^2 of sheet are mixed with water-absorbing materials and sandwiched between packaging materials.

As the ethylene gas adsorbent, bromine-adsorbed carbon molecular sieves, preferably those having 4-6 Å micropores and a particle diameter of 5-500 μm, which are obtained by adding sodium bromate- or potassium bromate-dissolved acidic water to activated carbon, reacting, drying, and pulverizing, are exemplified. These ethylene gas adsorbents are preferred since water has no influence, namely adsorbed ethylene gas is not released from them in the presence of water. Activated carbon, zeolites, Oyaishi (tuff), etc., which are generally used as ethylene gas adsorbents, are not preferred since they release adsorbed ethylene gas if water is present.

Beside those functional materials, other functional materials can be used, and their type is not particularly restricted.

Next, as water-absorbing materials, glucose, fructose, sucrose, maltose, lactose, sorbitol, maltitol, reducing starch hydrolyzate, locust-bean gum, tamarind seed gum, carrageenan, silica gel, zeolites, sodium chloride, calcium chloride, starch, graft polymers of acrylic acid salts, carboxymethylcellulose crosslinked members, vinyl alcohol-acrylic acid copolymer,

polyacrylonitrile hydrolyzate, crosslinked polyacrylic acid salts, modified polyvinyl alcohol, acrylic acid polymer, acrylic acid salt-acrylamide copolymer, isobutylene-maleic anhydride copolymer, etc. are exemplified. Other materials also can be used if they have high water absorptivity. It is also possible to use two or more of these materials together. The application quantity of water-absorbing polymer is 0.1-200 g and preferably 1-50 g per 1 m^2 of sheet.

To sandwich water-absorbing material between packaging materials, thermoplastic resins such as polyolefins, polyamides, polyesters, etc. and other suitable binders can be used.

The compositions for functional water-absorbing sheets of the present invention can be used as a form of coating agent (ink or paint) obtained by dispersing paint vehicles or printing ink vehicles. As solvents for the coating agents, aliphatic hydrocarbons, aromatic hydrocarbons, alcohols, ketones, esters, chlorine-containing hydrocarbons, nitrogen-containing hydrocarbons, or their mixtures, and organic solvents, which are used for ordinary paints and printing inks, are used.

As binders in the vehicles, natural or synthetic drying oils such as linseed oil, soybean oil, dehydrated castor oil, styrenated oil, vinyltoluenated oil, maleic oil, etc., natural or processed resins such as rosin, copal, dammar, shellac, hardened rosin, rosin ether, etc., synthetic resins such as polyvinyl acetate resin, polyvinyl alcohol, polyvinyl butyral, polystyrene resin, acrylic resin, phenolic resin, other modified resins, unsaturated polyester resin, alkyd resin, polyamide resin, epoxy resin, polyurethane resin, aminoplast resin, petroleum resin, etc., cellulose derivatives such as nitrocellulose, methyl-, ethyl-, carboxymethyl- or acetylbutyl cellulose, etc., rubber derivatives such as chlorinated rubber, cyclized rubber, etc., and binders, which are used in conventional paints or printing inks, such as glue, casein, dextrin, etc. can be used.

The content of water-absorbing polymer is generally 5-70% in the coating agent. If the content is less than the aforementioned range, the water absorbing capacity is not sufficient, and on the other hand, if it exceeds the range adhesion of water absorbing layers becomes insufficient. The content of binder may be 5-50% in the case of conventional paints or printing inks.

The coating agents to be used in the present invention contain specific functional materials as indispensable components, but if necessary, other known additives of various paints or printing inks, such as plasticizer, stabilizer, wax, grease, drying agent, drying aid, dispersant, thickening agent, filler, UV absorbent, etc. also can be used in the coating agents.

Water-absorbing sheets having specific function can be manufactured from the compositions of the present invention by the following method as an example.

Namely, a composition 3, containing a water-absorbing material and a binder, is uniformly spread on an internal layer 4 in Figure 1, and the other inner layer 2 is superposed and this is passed through hot emboss rolls to join them. Then, the joined base paper is cut to a fixed

size, stuffed between outer layers 1, 5 made of 3-way seal pouch, sealed, and passed through hot emboss rolls to obtain a water-absorbing sheet. Furthermore, as the inner and outer layers, not only a single layer but also a laminate comprising multiple layers can be used.

As the method of uniting the layers by passing through hot emboss rolls, methods of passing the layers

(1) between a hot emboss roll and a hot emboss roll,

(2) between a hot emboss roll and a hot roll,

(3) between a hot emboss roll and a roll,

(4) between a hot roll and a hot roll, or

(5) between a hot roll and a roll

are exemplified.

Water-absorbing sheets having specific functions manufactured using the compositions of the present invention are generally used, for instance, by directly inserting between fresh food items as a freshness-maintaining material for the fresh food in the case of packaging in cases, packaging in bags, tray packaging, etc., but in the case of easily dried food, it is possible to use the freshness-maintaining material in a wet state by absorbing water in it.

In addition, the water-absorbing sheets can be suitably processed and used for sanitary products, diapers, disposable mops, paper towels, etc.

Effect of the invention

As explained above, the freshness of fresh food can be simply maintained at a low cost without excess labor or time if the compositions of the present invention for water-absorbing sheets having specific functions are used. In addition, since a specific functional material is integrated with water-absorbing polymers, unique effects such as no danger of contamination of fresh food with functional materials such as an ethylene gas absorbent, antibacterial agents, etc. by breaking of bags, etc. can be expected.

In addition, it also has the merit of the capability of obtaining compositions for water-absorbing sheets having arbitrary functions according to the application purpose by suitably selecting specific functional materials and water-absorbing materials and mixing them.

Furthermore, when a water-absorbing material is sandwiched between a water-permeable packaging material and a water-impermeable material, namely a waterproof material, to integrate them in water-absorbing sheets made from the compositions of the present invention, the permeation of absorbed water at the rear surface of the water-absorbing sheets can be completely prevented in actual application so that a problem of conventional water-absorbing sheets is solved by a simple means to further enhance the value of the water-absorbing sheets, and thus their industrial application value is extremely high.

Next, application examples of the present invention are given.

Application examples

Application Example 1

A mixture containing activated carbon (White Eagle A, Takeda Chemical Industries Co., Ltd.) as deodorant, an organic acid-zinc oxide mixture (Daimushew 1300, Dainichiseika Color and Chemicals Manufacturing Co., Ltd.) 10 g/m^2 each, water-absorbing polymer (Aqua Keep 10SHP, Seitetsu Kagaku Co., Ltd.) 70 g/m^2, and binder [FLO-VAC (EVA powder), Seitetsu Kagaku Co., Ltd.] 10 mg/m^2 was uniformly spread on a paper sheet with a base weight of 25 g/m^2 (MSP25, Metel Co., Ltd.), and another paper sheet was put on it, then those were passed through hot emboss rolls to join them together (hot roll temperature 140°C, emboss pressure 5 kg/m^2).

The aforementioned base paper was cut to 320 x 200 mm, put into a trigonal seal pouch (size 330 x 210 mm) from nonwoven fabric with a base weight of 25 g/m^2 (Syntex PK105, Mitsui Petrochemical Industry Co.), and sealed tightly.

Comparative Example 1

A drip sheet containing no deodorant was manufactured by the same manner as in Application Example 1.

Experimental Example 1

Frozen horse mackerel was packed by the methods shown in Table 1, and after being stored in a refrigerator at 7°C for 3 days, the generation of drippage and odor were compared. Results are shown in Table 1.

Table 1

	Generation of drippage	Odor
Not packaged	A large amount of drippage generated	Malodorous
Comparative Example 1	None	Malodorous
Application Example 1	None	Almost odorless

It is understood from the results in Table 1 that when drip sheets of the present invention were used, there was neither drippage generation nor odor.

Application Example 2

A mixture containing a pulverized ethylene adsorption gas removing agent (Molsievon NGP6/8, Takeda Chemical Industries Co., Ltd.) 10 g/m^2, water-absorbing polymer (Aqua Keep 10SHP) 70 g/m^2, and binder (Kemit R272S, Toray Industries, Inc.) 0.5 g/m^2 was uniformly spread on a paper sheet with a base weight of 25 g/m^2 (MSP 25 of Metel Co., Ltd.), this was covered with a polyethylene-coated paper sheet (obtained by extrusion coating MSP 25 of Metel Co. with M-16P, Mitsui Nisseki Polymer Co., Ltd., at a thickness of 30 μm) by facing down the polyethylene coated side down, and this was passed through hot emboss rolls to join the sheets together (hot emboss roll temperature 160°C).

Then, water-absorbing polymer (Aqua Keep 10SHP, Seitetsu Kagaku Co., Ltd.) at 20 g/m^2 and binder (Kemit R272S, Toray Industries, Inc.) at 1.0 g/m^2 were spread on the polyethylene-coated paper side of the united paper sheet, this was covered with another paper sheet, and this was passed through hot emboss rolls to join the sheets (hot emboss roll temperature 160°C).

This was then cut to 320 x 210 mm, put on nonwoven fabric (NA240JP2096, Kuraray Co., Ltd.), and the nonwoven fabric was folded into the base paper side. Furthermore, nonwoven fabric was fed from the top, and the side was heat sealed by a gear roll. The end section was heat sealed by a seal bar. Furthermore, the whole part was united and cut at a side section.

Experimental Example 2

The sample of Application Example 2 was cut to 50 x 50 mm, put in a bottle (125 mL volume), and after ethylene gas was blown into the bottle at a concentration of 300 ppm, the bottle was closed. Then, the ethylene gas concentration was measured by gas chromatography.

Experimental Example 3

The sample of Application Example 2 was cut to 50 x 50 mm and put in a bottle (125 mL volume) to absorb water, and after ethylene gas was blown into the bottle at a concentration of 300 ppm, the bottle was closed.

Then, the ethylene gas concentration was measured by gas chromatography in the same manner as in Experimental Example 2.

Results of Experimental Examples 2, 3 are shown in Table 2.

Table 2

Time (h)	0	3	6	12	24
Experimental Example 2	326	99	41	ND	ND
Experimental Example 3	326	117	45	ND	ND

(Unit: ppm)

Application Example 3

A mixture containing a pulverized (average particle diameter 25 μm) ethylene gas adsorption agent (Molsievon NGP6/8, Takeda Chemical Industries Co., Ltd.) 20 g/m^2, water-absorbing polymer (Aqua Keep 10SHP, Seitetsu Kagaku Co., Ltd.) 70 g/m^2, and binder [FLO-VAC (EVA powder), Seitetsu Kagaku Co., Ltd.] 10 g/m^2 was uniformly spread on a paper sheet with a base weight of 25 g/m^2 (MSP25, Metel Co., Ltd.), this was covered with another paper sheet, and this was passed through hot emboss rolls to join the sheets together (hot emboss roll temperature 140°C, embossing pressure 5 kg/cm^2).

The above base paper was then cut to 320 x 210 mm, packed into a trigonal seal pouch (size 330 x 210 mm) of nonwoven fabric with a base weight of 25 kg/m^2 (Syntex PK105, Mitsui Petroleum Industry Co.), and sealed.

Comparative Example 2

A freshness-maintaining material for vegetables and fruits was manufactured in the same manner as in Application Example 1, except that the ethylene gas removing agent was not added.

Experimental Example 4

10 nests from Tokuyama Prefecture were each wrapped up and bagged by the methods shown in Table 3 and stored at 5°C for 3 months. Results are shown in Table 3.

were washed away in 100 mL sterilized water containing 0.1% Tween 80, and the number of live bacteria in the sterilized water was measured by an ordinary mixed diluted plate culture method using an ordinary agar culture medium (from Eiken Kagaku Co.) in the case of *Bacillus subtilis* and a potato dextrose agar culture medium (from Eiken Kagaku Co.) in the case of *Aspergillus niger*, and the number of live bacteria adhered to each sheet was calculated. Results are shown in Table 4.

Table 4

Tested bacteria	Sample	Immediately after spraying (No. of bacteria/25 cm^2)	After storing at 22°C for 7 days (No. of bacteria/25cm^2)
Bacillus subtilis	Application Example 4	$6.2x10^4$	below 300
	Comparative Example 3	$5.5x10^4$	$3.2x10^6$
	Comparative Example 4	$5.3x10^4$	$2.4x10^3$
Aspergillus niger	Application Example 4	$7.7x10^4$	below 300
	Comparative Example 3	$6.3x10^4$	$4.4x10^5$
	Comparative Example 4	$7.8x10^4$	$1.1x10^3$

It is seen from Table 4 that the antibacterial water-absorbing sheet of the present invention has notable antibacterial action as compared with Comparative Example 3 (no antibacterial zeolite) and Comparative Example 4 (no water-absorbing resin).

Brief description of the figure

Figure 1 is a cross-sectional view of a freshness-maintaining material as an application example of the present invention

1.....Nonwoven fabric (outer layer)

2.....Paper (inner layer)

3.....Composition comprising a water-absorbing material and a deodorant

4.....Paper (inner layer)

5.....Nonwoven fabric (outer layer)

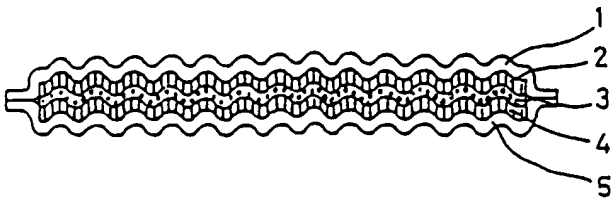

Figure 1